Thermal and Electrical Properties of Rare-Earth Sulfides At High Temperatures

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In the past few years there has been renewed interest in the semiconducting rare-earth sulfides (Ln_3S_4, Ln_2S_3) (Ln, Pr, Nd, Gd, Dy), with the Th_3P_4-type structure (defective structure - $Ln_{3-x}\,V_x\,S_4$ where V_x is the the rare-earth's vacancies at cationic sublattice). The high melting points (T > 2100 K), low thermal conductivity (1.5-3.5 $W{\cdot}m^{-1}\,K^{-1}$) and the electrical conductivity changing continually from a metallic conductivity to a semiconductor with an increase in the number of vacancies V_x make them good candidates as potential high-temperature thermoelectric materials. The results of our investigations of the temperature dependence (300-1200 K) of the thermal and electrical conductivity (λ, σ), the thermal expansion coefficient and heat capacity (α, C_p) of the rare-earth sulfides $Ln_{3-x}\,S_4$, (Ln, Pr, Gd, Dy) (x=0; 0.209; 0.232; 0.26; 0.28; 0.33) are presented. The temperature dependence of the lattice (λ_L) and electronic (λ_e) contributions to the total thermal conductivity are determined. The total thermal resistivity is $W=W_1+W_2+W_3$. W_1- is the thermal resistivity caused by phonon-phonon scattering, W_2 is the thermal resistivity caused by scattering on the vacancies; and W_3 is the scattering on mass defect and change of elastic parameters. W_1 and W_2 are independent of temperature. The temperature dependence of the lattice thermal conductivity of the investigated compounds is described by an equation $\lambda \sim T^{-n}$ (n=0.95-0.5).

The lattice thermal conductivity from $Ln_{3-x}\,S_4$ to $Dy_{3-x}\,S_4$ is decreased. It is caused by the increase of the atomic weight and additional increase of the anharmonicity of thermal oscillations of a lattice. It is confirmed also by the dependence of the thermal expansion coefficient on composition that increases from $Ln_{3-x}S_4$ to $Dy_{3-x}\,S_4$ with a decrease of the sound velocity The accuracy correlation between the lattice thermal conduc-tivity and the thermal expansion coefficient for all compounds are observed. The electrical resistivity may be described as $\rho(T)=\rho_0+\rho_1(T)$ where ρ_0- is the resistivity caused by scattering of electrons on the cationic vacancies and ρ_1- is caused by scattering on the thermal oscillations of the lattice.